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(71) Applicant(s)

Richard William Keatch
Unit 27, Frederick St Centre, ABERDEEN, AB2 1HY,
United Kingdom

(72) Inventor(s)

Richard William Keatch

(74) Agent and/or Address for Service

Urquhart-Dykes & Lord
8th Floor, Tower House, Merriion Way, LEEDS,
LS2 8PA, United Kingdom

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E21B 37/06, C23G 1/24

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E1F FPE

C7E E124 E170 E188 E3B

(56) Documents Cited

GB 1469460 A GB 1293440 A US 5366016 A
US 5183112 A

(58) Field of Search

UK CL (Edition O) C7E, E1F FPE
INT CL⁶ C23G, E21B

(54) Removal of sulphate scale from surfaces

(57) A method for dissolving sulphate scale comprises contacting the sulphate scale with a solution containing a scale convertor, e.g. potassium carbonate; a catalyst, e.g. potassium formate; and a chelating agent.

GB 2 314 865 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

DISSOLUTION RATE OF BARIUM SULPHATE POWDER WITH
DIFFERENT DTTPA FORMULATIONS (0.5M) 60C.

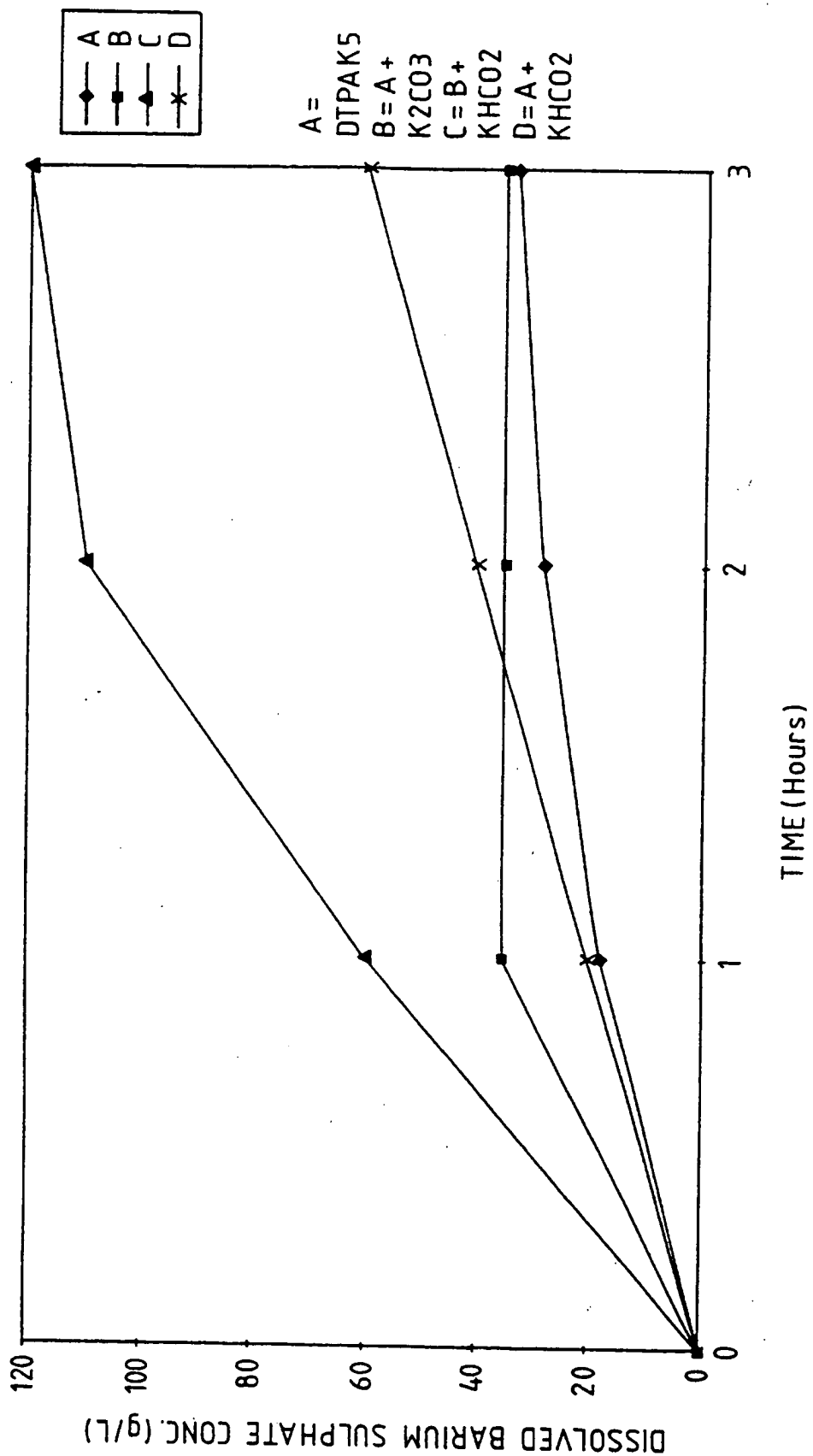


FIG. 1

DISSOLUTION RATE OF BARIUM SULPHATE POWDER AS A
FUNCTION OF TEMPERATURE WITH NEW DISSOLVER

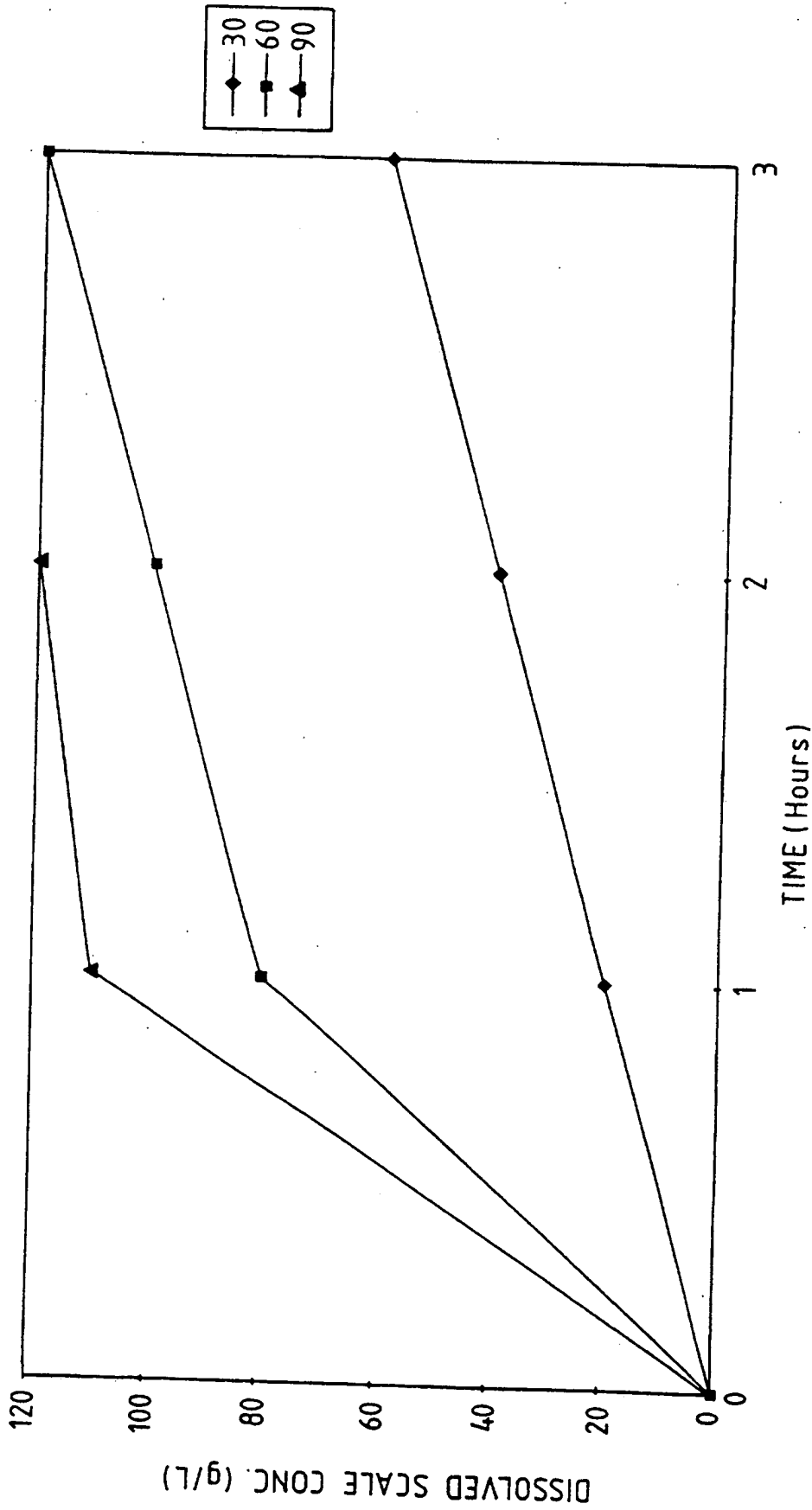


FIG. 2

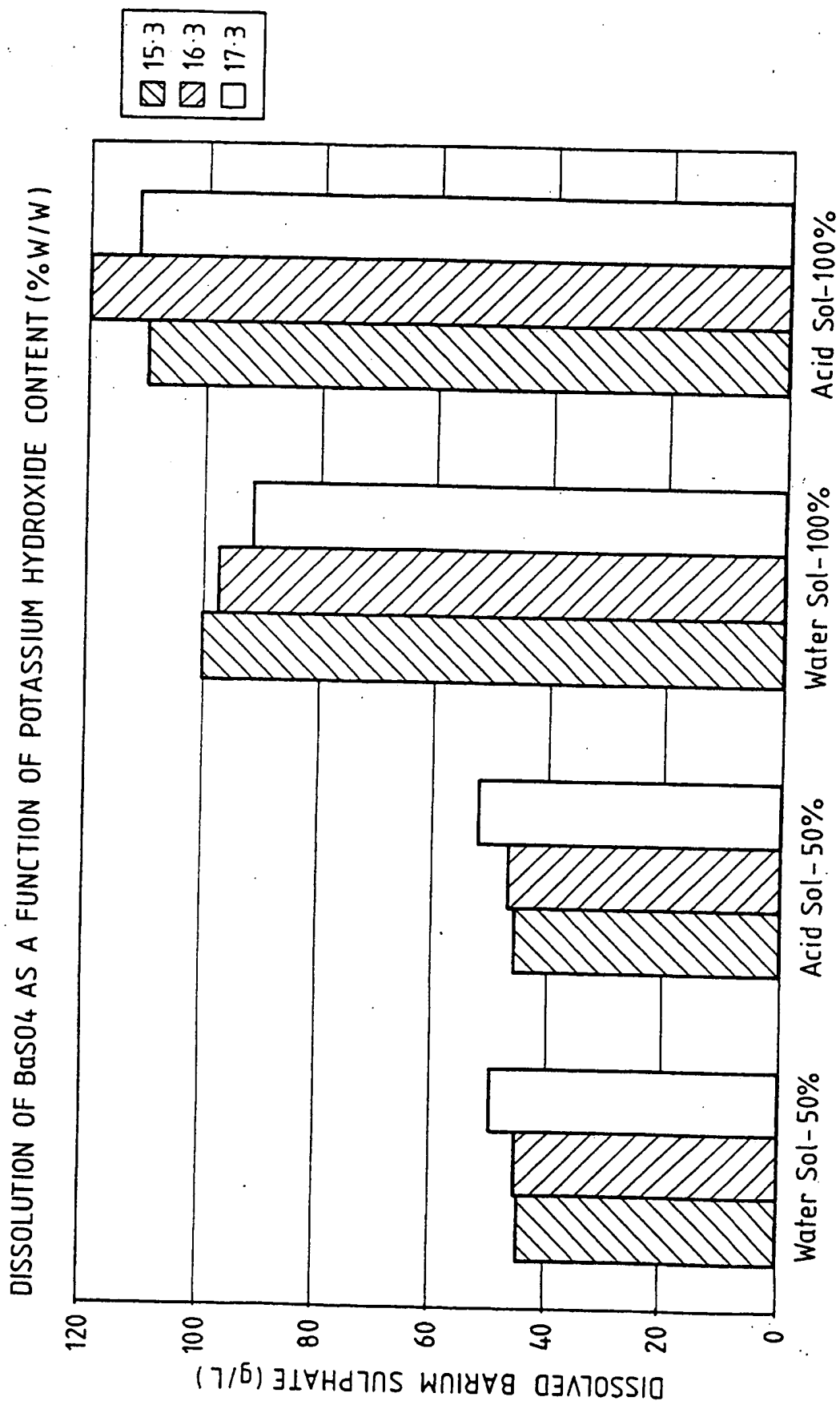


FIG. 3

DISSOLUTION OF BaSO_4 AS A FUNCTION OF CATALYST CONCENTRATION

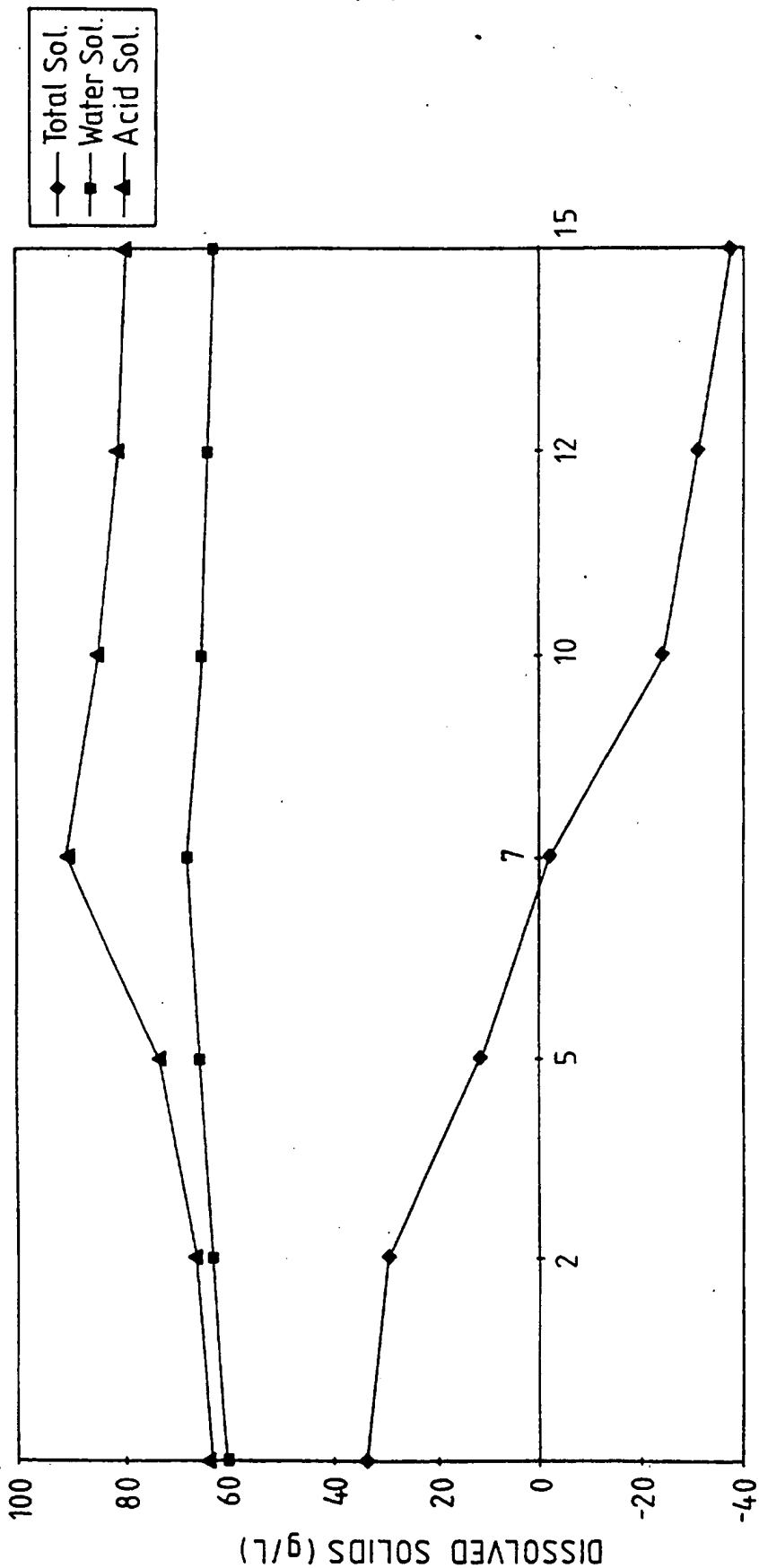


FIG. 4

SULPHATE SOLUBILISATION FROM BARIUM SULPHATE
USING POTASSIUM CARBONATE pH11, 60C

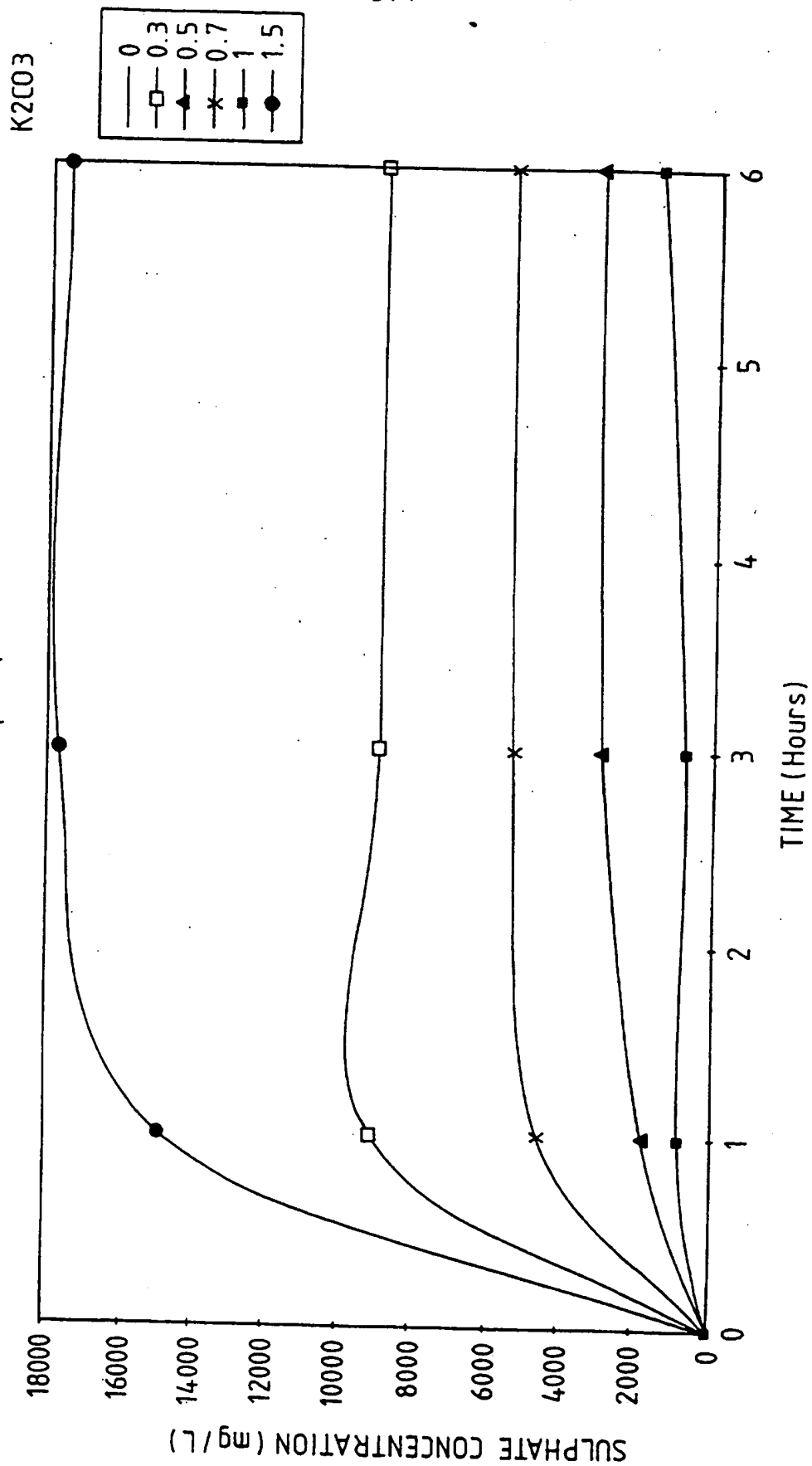


FIG. 5a

SULPHATE SOLUBILISATION FROM BARIUM SULPHATE
USING POTASSIUM CARBONATE pH11, 90C

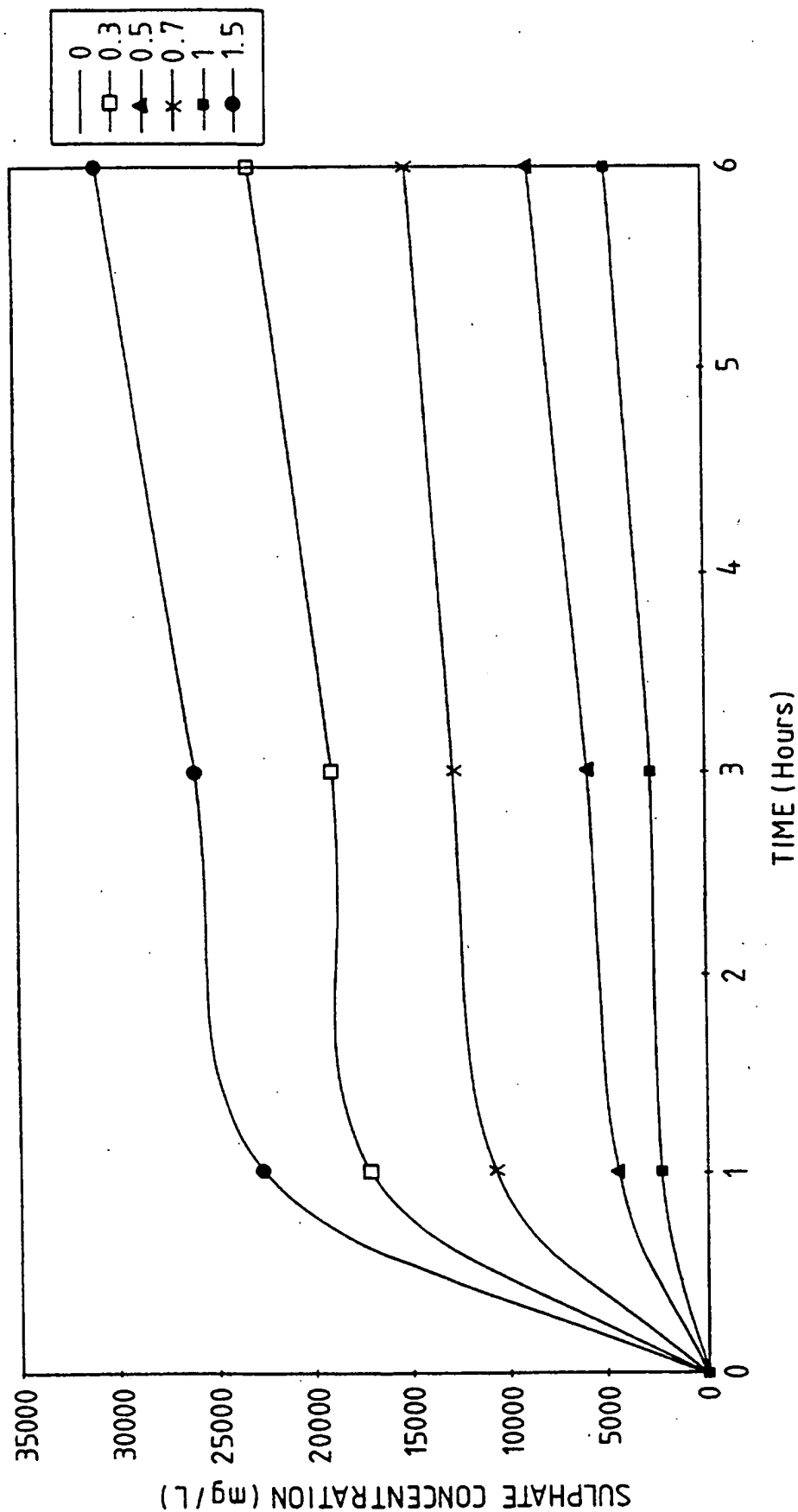


FIG. 5b

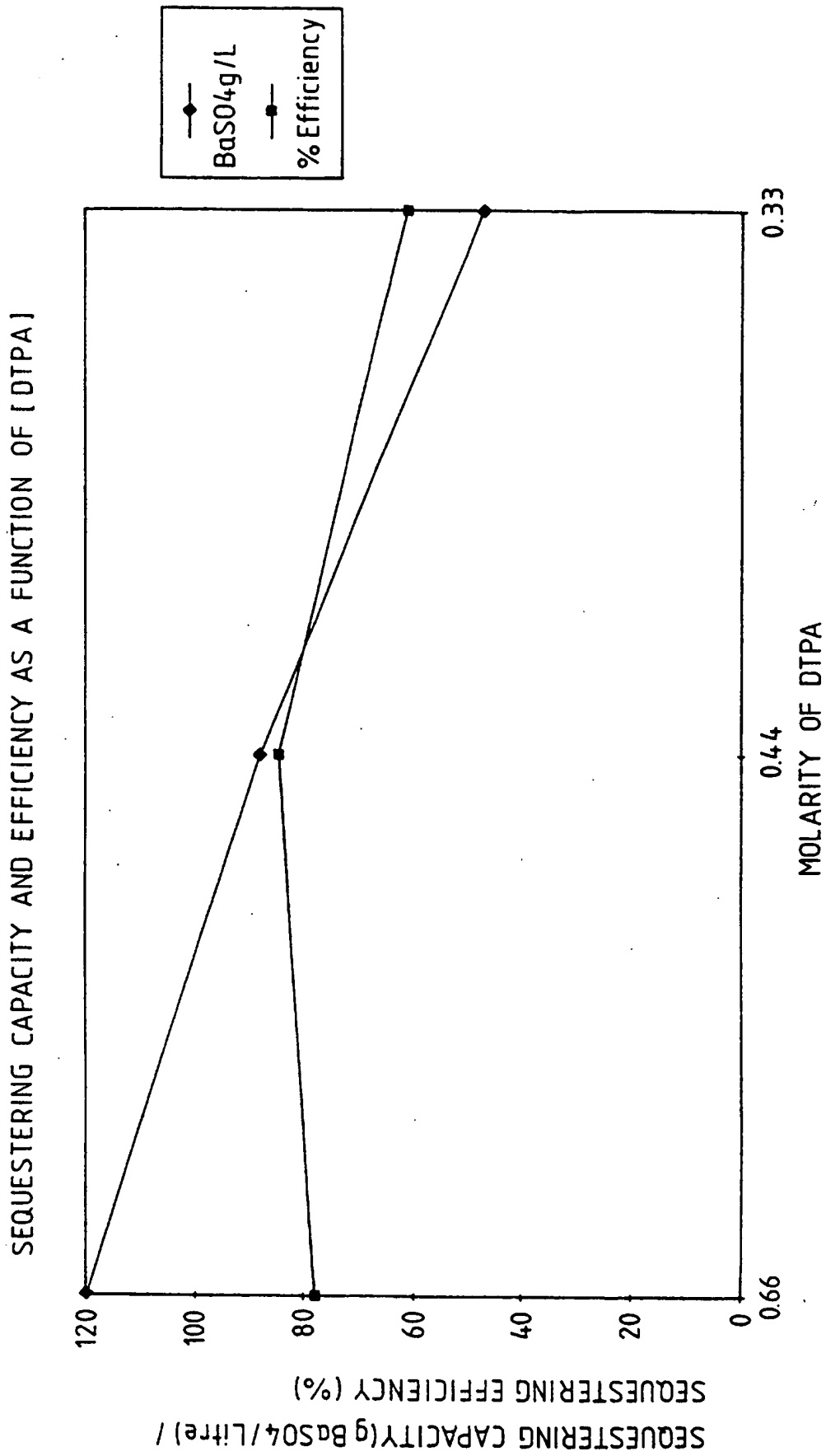


FIG. 6

REMOVAL OF SCALE FROM SURFACES

This invention relates to the removal of scale from surfaces and provides a method of removing scale from a surface, and solutions for treatment of a surface to remove scale. The invention is particularly, but not exclusively for use in oil and gas wells.

In oil and gas well operations, water insoluble scale is formed in tubing, casings and associated equipment, as well as the wellbore and the subterranean formation itself which carry at least in part, water or brine waters. These waters have the potential to form water insoluble mineral scale species such as barium sulphate, strontium sulphate, calcium carbonate, iron carbonate, iron oxides, iron sulphides and magnesium salts. There is also a potential for water insoluble scale to be produced by the introduction of various treating chemicals such as phosphonic acid and polycarboxylic acid scale inhibitors which can form damaging calcium and iron salts if applied incorrectly.

Scale formation can occur as a result of a change in pressure or temperature or both in the system or can result from the mixing of incompatible waters such as formation water containing barium, strontium and calcium with sulphate rich seawater associated with water flooding methods of secondary recovery where water is injected into the formation rock to maintain reservoir pressure as oil is produced.

Formation water is the natural water found within the pores of the formation rock along with the oil and gas. The water is rich in metal ions such as calcium, barium and strontium which have been leached from the naturally occurring minerals in the rock.

The precipitation of scale can occur in the pores of the reservoir rock and throughout the entire process train.

The process train is a series of pipes, separators, coolers, pumps and other equipment on the oil platform involved in processing the mixture of oil, water and gas flowing from the wells so that dry gas and oil can be extracted from the mixture and individually exported via sub sea pipelines to refineries.

Scale build up decreases reservoir production and efficiency of process equipment operation. The need to maintain high production rates makes scale formation a serious problem and remedial action is required in the form of preventative action involving scale inhibitor treatment or removal when scale has already formed.

The chemical removal of carbonate scale has traditionally been carried out using acids, either mineral acid or carboxylic acids which react with the scale rapidly to form carbon dioxide and a solution of calcium salt.

The chemical removal of sulphate scale is more difficult since the scale has to be dissolved using chelating agents and both the rate of dissolution and the levels of scaling cation which can be sequestered is limited.

According to the present invention there is provided a method for dissolving sulphate scale, the method comprising the steps of:

contacting the sulphate scale with a solution containing scale converter, catalyst and chelating agent.

The scale converter ionises the insoluble scale. The catalyst increases the efficiency of sequestration of the scaling cation. The chelating agent complexes with cations of the scale in solution.

Preferably, the catalyst is potassium formate.

The preferred salt of each component is the potassium salt although caesium salts may in some circumstances offer benefits due in large to their greater solubility in water.

The preferred alkalinity for barium and strontium sulphate dissolution is in the range 10 to 13.

Advantageously the alkalinity is pH 12.

The preferred alkalinity for calcium sulphate is in the range 7 to 9 and advantageously pH 8.5 when DTPA is used as the chelating agent.

Other carboxylic acids have been found to have a catalytic effect, for example, oxalic acid and salicylic acid but the effect of these other carboxylic acids is not so great as the formic acid salt.

The low molecular weight of the formate, and the high solubility of alkali metal and divalent formate salts result in the formate being the most effective catalytic carboxylate. Alternative converters include bicarbonate. The effectiveness of bicarbonates particularly on barium and strontium sulphate scale has been found to be much less than that of potassium carbonate, however in some instances bicarbonate could be used for calcium sulphate scale conversion.

Alternative chelating agents could be selected from the groups comprising the polyaminopolycarboxylic acids and the crown ethers. The choice is related to the specificity of the chelating agent towards the particular scaling cation, the logK value, the optimum pH for sequestering and the commercial availability of the chelating agent. More specifically, for strontium sulphate there are certain performance advantages in using 1,2-Diaminocyclohexanetetraacetic acid or triethylene, triaminetetraacetic acid or triethylenetetraminehexaacetic acid. For calcium sulphate, ethylenediaminetetraacetic acid is an alternative although the dipotassium salt is preferred over the tetra potassium salt.

The use of chelating agents for the dissolution of sulphate scale was first accomplished using ethylenediaminetetraacetic acid (EDTA) sodium salts. The development of more efficient scale dissolvers addressed the use of potassium salts and other chelating agents. To this end, the most cost effective current treatments involve the application of pentapotassium diethylenetriaminepentaacetic acid (DTPA) solutions.

The inventor has surprisingly found that the use of potassium carbonate as a converting agent can markedly improve the dissolution rate of sulphate scale, although the overall sequestering capacity of the chelating agent is unaffected.

Potassium carbonate when used as a converting agent acts on barium sulphate scale such that surface barium sulphate is converted to form barium carbonate (in solid form) and potassium sulphate (aqueous form).

The solubility of barium sulphate in boiling water is

only 0.0004g/100mls. The conversion to barium carbonate by exposure of the sulphate scale surface to a high concentration of potassium carbonate increases the solubility to approximately 0.0065g/100mls at 100C so that at any one time there should be a barium ion concentration of 45mg/L available for the chelating agent to sequester.

Since the barium ion concentration associated with barium sulphate is only about 2.35mg/L the barium can be sequestered at a rate up to 19 times higher in the presence of the carbonate converting agent.

The increased dissolution rate afforded by the incorporation of converting agents into dissolver formulations by means of the present invention has allowed downhole sulphate scale to be removed in a time efficient manner where the scale accumulations have been of moderate thickness (1-10mm), but the limited sequestering capacity of chelating agents has restricted the number of applications where chemical removal alone can be used as a remedial treatment.

The use of carbonate converting agent has an additional beneficial effect on the amount of scale which can be removed with a given volume of dissolver particularly where scale exists in a particulate form and downhole conditions of carbon dioxide partial pressure and / or organic acids provide acid conditions for produced water which allows converted, unchelated scale to be removed after the well has been returned to flowing conditions.

Produced water refers to commingled seawater and formation water. This mixing of waters can result in mineral scale deposition since the seawater is rich in sulphate and the formation water rich in cations.

The inventor has found that certain carboxylic acids can be used together with converting agents to increase the efficiency of chelation of cations by the sequestering agent so that the effective sequestering capacity of the dissolver is increased.

The efficiency of sequestration is measured as the percentage of total chelating agent which at equilibrium is

present as the scale metal chelate. Typically, the sequestering efficiency is only of the order of 30-50% under usual chelating agent application concentrations (5-20% w/w). We have found potassium formate to be particularly effective in increasing the efficiency of chelation of barium by DTPA so that efficiencies of over eighty five percent can be achieved.

It is believed that the mechanism by which the formate ion achieves this effect is that two formate ions bind with a barium ion transiently and increase the subsequent efficiency of chelation by DTPA. Under high surface area to volume ratio conditions with converting agent and chelating agent only present, it has been observed that the release of potassium sulphate outstrips the sequestration of barium ion. It is further believed that there comes a time during dissolution when the alkali metal sulphate concentration is sufficient to prevent further barium ion chelation due to the effects of mass action so that despite the high logK value for the chelate the tendency for barium sulphate to reform is higher and the full sequestering capacity of the chelating agent is never utilised.

The presence of excess formate ion may push the equilibrium in favour of barium chelate formation so that the increasing dissolved sulphate cannot effectively compete with the formate and chelating agent for the available barium ions in solution. By careful choice of the relative amounts of chelating agent, converting agent and catalyst the optimum dissolution rate and sequestering capacity of the dissolver can be achieved for a particular application.

The situation with field scale is different since the surface area of layered scale accumulations on pipework offers a limited surface area for the converting agent to attack. Fresh surface to convert will only become available as the chelating agent sequesters the barium ion.

The term field scale is used to identify the mineral scale found in the oil field as opposed to pure analytical grade reagent powdered mineral. The scale that forms in "the field" tends to consist of cylindrical crystalline layers of varying chemical composition, morphology and permeability. The

crystalline layers are generally cylindrical because they are most often encountered on internal surfaces of pipes.

In this instance, therefore, the rate limiting step is the chelation of barium ions and the chelating efficiency of a solution comprising converting agent and chelating agent for this type of scale is likely to be higher than for powdered analytical grade reagent barium sulphate particularly at high temperature and high dissolver concentration where the conversion process is enhanced.

In other words, although the dissolution rate of layered crystalline scale will be slower due to the lower surface area when compared with particulate scale, the efficiency of sequestration will be relatively higher due to the converting agent being restricted in its effect.

The damage caused to production downhole is most frequently attributable to a limited amount of scale in the critical oil producing zone in the near wellbore. This scale will typically consist of a thin layer of scale and scale particles in the formation rock pores. In these instances, the advantage of the new scale dissolver formulation will be significant. In the removal of scale in production tubulars the amount of scale required to form a significant flow restriction is much greater and the improved sequestering capacity of the new dissolver will enable the scale to be removed with less chemical and fewer soak/displacement operations.

The term "near wellbore" refers to the area of the reservoir where oil is being produced. A well usually consists of a steel lined hole which is several inches in diameter and which has been drilled through oil bearing rock down to a depth of several thousand feet. The steel casing is perforated using explosive charges in the layers where oil is situated to allow the oil to flow up the tubing to the surface platform. Near wellbore refers to the area around the perforations and a few feet into the reservoir.

An additional benefit of the new dissolver has been noticed during a new dissolver application method involving the

use of ultrasound.

An ultrasonic tool may be used which will enhance dissolution rates by increasing surface agitation and also increasing the contact of fresh dissolver in pores within the scale by creating a pressure wave which forces dissolver in and out of the scale and prevents dissolver becoming saturated in the low mixing potential areas. The increased effective surface area during sonication of scale allows the new dissolver to act much more efficiently, resulting in dissolution solution rates fifteen times greater than that of non-sonicated solutions with layered crystalline scale accumulations. The benefits of the dual converter, catalyst action in promoting faster dissolution and increased sequestering capacity are maximised under ultrasonic conditions.

Experiments

The following experiments were carried out to show the unexpected performance advantages of combining both converting agent and catalyst with chelating agent according to the present invention and to identify the preferred proportions of the various chemical components.

The pattern of solubilisation of barium sulphate has been examined by plasma emission analysis of barium, potassium and sulphate levels in dissolver solutions as a function of time, temperature dissolver concentration and scale mass to dissolver volume ratio. The scale mass has been determined as a function of time and the solubility of the deposit in both water and weak acid examined following treatment with scale dissolver.

1. Comparison of sequestering capacity of DTPA penta potassium salt, in the presence of potassium carbonate, potassium formate, and both potassium carbonate and potassium formate at 60 degrees Centigrade.

2. The pattern of solubilisation of barium and sulphate ions of powdered barium sulphate with the new dissolver formulation as a function of temperature

3. The effect of potassium hydroxide concentration on the performance of the dissolver formulation in dissolving powdered barium sulphate. The addition of alkali allows firstly the formation of the penta potassium salt of DTPA acid and any excess allows the effect of the free potassium hydroxide on dissolution performance to be compared.

4. Optimum concentration of catalyst in the new dissolver. The effect of a range of potassium formate concentrations on the efficiency of dissolution was studied by incubating the various solutions at 60C and taking samples for barium and sulphate ion analysis. At the end of the experiment the remaining precipitate was filtered through a 0.45 micron Millipore filter, dried at 100C and weighed. This deposit was then water washed, filtered, dried and weighed before acid washing in 10% formic acid, filtering, drying and reweighing.

5. Optimum concentration of converter in the new dissolver. A range of different molarity solutions of potassium carbonate solution were prepared and a mass of powdered barium sulphate added to the solution to give a 1M mixture. The conversion of barium sulphate to potassium sulphate and barium carbonate was measured at regular time intervals.

6. Optimum concentration of chelating agent in the new dissolver. The sequestering capacity of a range of chelating agent solutions was compared with the sequestering efficiency up to the solubility limit of the dissolver components. Each component was added at its optimum concentration as measured in the previous tests. The sequestering efficiency was measured as the proportion of barium chelate to the total chelate concentration.

The invention will now be further described by way of example only with reference to the following drawings in which:

Figure 1 is a graph showing the dissolution rate and sequestering capacity of DTPAK5, DTPAK5/K₂CO₃, DTPAK5/KHCO₂ and DTPAK5/K₂CO₃/KHCO₂ respectively. The speed of dissolution and the sequestering capacity of the combined converting agent / catalyst formulation is much greater than for any of the other solutions;

Figure 2 is a graph showing the rate of dissolution as a function of temperature. The rate of dissolution is seen to increase with increasing temperature but the rate of solubilisation at lower temperatures is much greater than has been achieved in the past with existing formulations;

Figure 3 is a graph showing that at lower dissolver concentrations there is a benefit in having an excess of around 2% w/w KOH. With neat dissolver there appears to be some advantage in having a reduced excess of 1% w/w or perhaps no excess at all in terms of sequestering capacity but the rate of dissolution of powdered barium sulphate in all cases increases with increasing potassium hydroxide concentration.

It has been found however that the effect of potassium hydroxide is highly variable with oilfield scale samples and each case needs to be looked at independently where possible in order to optimise the pH for a particular scale problem;

Figure 4 is a graph showing details of the effect of a range of catalyst concentrations on the dissolution rate and the sequestering capacity of the various dissolver solutions and the effect on soluble salt speciation during the treatment.

It can be seen that at low catalyst concentrations there is a weight loss of solids whereas for higher concentrations of potassium formate there appears to be an overall weight gain. The increased mass represents precipitated potassium sulphate which is water soluble but forms as a by-product of the conversion and chelation reactions as its solubility limit is exceeded. There appears to be a peak in total sequestering capacity at around 7%w/w which is further enhanced when acid soluble barium carbonate material is taken into account;

Figures 5(a) and (b) are graphs showing the degree of conversion of barium sulphate to barium carbonate at a range of potassium carbonate concentrations. At all temperatures there appears to be a benefit in having high concentrations of converting agent. The effect is however greater at lower temperature and the problem of incorporating many water soluble active components all competing for the available water into one formulation requires the solubility limit of each of the

components and their effectiveness in solubilising the sulphate scale to be balanced; and

Figure 6 is a graph showing the sequestering capacity and efficiency as a function of chelating agent concentration related to optimum converter and catalyst concentrations. The sequestering capacity of the dissolver appears to peak close to the solubility limit of DTPA in the formulation whilst the efficiency of sequestration peaks at a DTPA concentration of around 0.44M under the adopted test conditions.

The effect of a range of potassium formate concentrations on barium sulphate conversion to potassium sulphate and barium formate was studied and found not to be significant at a pH of 11 and a temperature of 60 degrees Centigrade.

A preferred formulation for the new barium sulphate scale dissolver is by weight:

- 20.00 percent Diethylenetriaminepentaacetic acid
- 16.33 percent potassium hydroxide
- 14.85 percent potassium carbonate
- 10.39 percent potassium formate
- 38.43 percent water.

Page 10 - GB 2314865
10261
- 25, 28, 32, 55, 56

CLAIMS:

1. A method for dissolving sulphate scale, the method comprising the steps of:
contacting the sulphate scale with a solution containing scale converter, catalyst and chelating agent.
2. A method according to claim 1, wherein the catalyst is potassium formate.
3. A method according to claim 1 or claim 2, wherein the preferred alkalinity for barium and strontium sulphate dissolution is in the range 10:13.
4. A method according to any one of claims 1 to 3, wherein the alkalinity is pH 12.
5. A method according to any one of the preceding claims, wherein the preferred alkalinity for calcium sulphate is in the range 7 to 9.
6. A method according to any one of claims 1 to 4, wherein the alkalinity or calcium sulphate is pH 8.5 when DTPA is used as the chelating agent.
7. A method as substantially hereinbefore described with reference to the accompanying drawings.



Application No: GB 9713383.9
Claims searched: 1-7

Examiner: David Pepper
Date of search: 18 September 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): E1F FPE; C7E

Int Cl (Ed.6): E21B; C23G

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 1469460 A (Borg-Warner Corp) - See page 2, lines 66-86	1-6
X	GB 1293440 A (F.J.Quattrini) - See page 2, lines 89-99	1-6
Y	US 5366016 A (Mobil Oil Corp) - See col 3, lines 11-19	1-6
Y	US 5183112 A (Mobil Oil Corp) - See col 2, lines 46-68	1-6

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.